UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND PHYSICOCHEMICAL INVESTIGATIONS OF TEMPLATED AND COMPOSITE ZINC OXIDE

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By

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chair: Prof Mohd Zobir Bin Hussein, PhD

Faculty: Science

The diversity in shapes and dimensions as well as the hollow structures of zinc oxide (ZnO) from nano-to-microscale has attracted interests in its application as promising materials in driven to multifunctionality of performance and distinct domain of applications. Morphology-controlled synthesis of nano-to-micrometer dimensions of inorganic materials has become a routine in recent nanotechnology research efforts. Among several techniques attempted, templated synthesis approach is the most widespread route used by many scientists nowadays to prepare a wide variety of nanostructured and hollow-structured materials. However, this approach is usually complicated and requires stringent experimental conditions. Therefore, the use of microbial cells as templating agent is highly appealing. Nonetheless, to develop this facile and environmental-friendly method in preparing metal oxide particles still remains an insignificantly explored discipline. Another challenge in this materials research is also to find a proper way to overcome over the aggregation/agglomeration of ZnO

particles with a minimum of chemicals used and more environmental-friendly products are produced.

Nano- and micro-structured ZnO with specific shapes and dimensions was synthesized via hydrothermal method using live and dead *Bacillus cereus* bacterium as a biotemplating agent, without adjusting the pH of the system. ZnO particles with raspberry-, plate- and hollow rod-like particles have been successfully synthesized through this method and possible mechanism on the formation of ZnO structures have been proposed. Various volume ratios of metal ion solutions with respect to the bacterial suspensions have been studied to investigate their effects on the morphology architecture of ZnO nano/microparticles. Volume ratio at 20:10 was observed to be the optimum condition for biochemistry process to occur in the live bacterial cell for the formation of well-ordered ZnO nanostructures. On the other hand, volume ratio of 10:10 was found to be the ideal concentration for the construction of perfect hollow rod-like ZnO microparticles.

The calcined sample of ZnO obtained from the biochemistry process occurring in live bacterial cell; shows that the raspberry-like structure is composed of 20-30 nm nodules and the plate-like structure has the thickness of about 25 nm as confirmed by FESEM micrographs. AFM 3D topographies and FT-IR elucidation confirmed that the reaction had occured between free Zn^{2+} cations and the deprotonated outer bacterial surface functional groups. The ZnO synthesized using dead bacterial cell as the biotemplating agent shows that the ZnO has nucleated on the dead *B. cereus* cell body during the hydrothermal reaction, before the sample was subjected to the heat treatment at 500 °C.

These results show that the size and shape of the ZnO nano/microstructures would depend on the organelles that the zinc species were templated on and amount of zinc species introduced into the bacterial suspension system.

Another topic investigated is the study on the behaviour of ZnO particles aggregation/agglomeration in ZnO/PVA polymer composite films prepared at various % (w/v) of PVA and different mass ratios of ZnO powder to PVA polymer without the use of organic capping agent as particle stabilizer. Several ZnO to polymer mass ratios have been prepared using commercial ZnO powder and water-soluble polymer, polyvinyl alcohol (PVA) via solution casting method. The thermal analyses (TGA-DTG and DSC) show that the thermal stability of polymer, PVA deteriorated after embedding ZnO particles and become significant when higher ZnO amount was incorporated into PVA matrix. From XRD of ZnO/PVA composite films, the observed diffraction intensities of ZnO and PVA phases were found to be depending on the particles aggregation and the contents of ZnO powder and PVA polymer. The band gap energy, E_g of the composite films obtained by UV-Vis analysis was found to decrease when the ZnO and PVA contents increased. This may be due to the formation of larger ZnO particles because of the high tendency of the particles to aggregate together. In addition, the possibility of ZnO particles could be well-dispersed inside PVA matrix is promising at relatively low ZnO and PVA contents. This was confirmed by visualization of ZnO distribution in the mass ratio of ZnO to PVA at 1:30 in 1% PVA matrix through TEM and ESEM micrographs.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN KAJIAN FIZIKOKIMIA KE ATAS TEMPLAT DAN KOMPOSIT ZINK OKSIDA

Oleh

WAN HAIZUM BINTI WAN NOR AZMIN

Februari 2011

Pengerusi: Profesor Mohd Zobir Bin Hussein, PhD

Fakulti: Sains

Kepelbagaian dalam dimensi dan struktur berongga bagi nano/mikrostruktur zink oksida (ZnO) telah menjadikan bahan ini sebagai bahan penting dalam pelbagai aplikasi dan fungsi. Oleh kerana itu, kaedah kawal-morfologi dalam sintesis nano/mikrostruktur bagi sesuatu bahan tak organik telah menjadi satu rutin dalam usaha penyelidikan nanoteknologi masa kini. Di antara teknik-teknik yang biasa digunakan oleh para saintis adalah pendekatan secara sintesis templat yang ternyata sukar dan selalunya memerlukan keadaan eksperimen yang ekstrim. Maka, penggunaan sel mikrob sebagai agen templat adalah sangat menarik perhatian. Walaubagaimanapun, bagi membangunkan kaedah yang mudah dan mesra alam ini dalam sintesis partikel logam oksida masih belum dikaji sepenuhnya. Cabaran lain yang juga dihadapi dalam penyelidikan ini adalah untuk mencari penyelesaian yang sesuai bagi mengatasi masalah agregasi/aglomerasi partikel ZnO dengan menggunakan bahan kimia pada kadar yang minima disamping dapat menghasilkan produk yang lebih mesra alam.

Dalam kajian ini, sintesis bagi spesifik bentuk dan dimensi nano/mikrostruktur ZnO adalah melalui kaedah hidrotermal mudah dengan menggunakan sel hidup dan sel mati bakteria *Bacillus cereus* sebagai agen biotemplat. pH sistem dalam sintesis ini dikekalkan sepanjang eksperimen dijalankan. Partikel ZnO dengan struktur rasberi, plat, dan rod berongga telah berjaya disintesis melalui kaedah ini dan mekanisme yang mungkin bagi pembentukan struktur-struktur partikel ZnO ini telah dicadangkan. Beberapa nisbah isipadu larutan ion logam kepada larutan ampaian bakteria telah dikaji kesannya terhadap pembentukan morfologi nano/mikropartikel ZnO. Nisbah isipadu pada 20:10 adalah merupakan keadaan optimum bagi proses biokimia berlaku di dalam sel bakteria hidup bagi pembentukan lengkap nanostruktur ZnO. Manakala nisbah isipadu pada 10:10 adalah merupakan kepekatan yang sesuai bagi pembentukan sempurna struktur berongga mikropartikel ZnO. Partikel ZnO hasil daripada sintesis ini telah dilakukan penciriannya dengan menggunakan kaedah XRD, SEM, FESEM, AFM, TEM, dan FT-IR.

Berdasarkan data-data yang dikumpul, ZnO yang diperoleh daripada proses biokimia yang berlaku di dalam sel bakteria hidup setelah dikalsin, ZnO dengan struktur rasberi adalah didapati terbentuk daripada nodul-nodul yang bersaiz antara 20-30 nm dan struktur plat pula mempunyai ketebalan lebih kurang 25 nm setelah dilakukan pencirian FESEM. Topografi AFM dan analisis FT-IR telah membuktikan bahawa tindakbalas antara kation zink bebas dan kumpulan berfungsi daripada permukaan bakteria yang telah ternyahproton adalah berlaku. Manakala ZnO yang diperoleh daripada sel bakteria mati, analisis melalui XRD dan pemetaan EDX menunjukkan bahawa ZnO telah nukleat di sekeliling badan sel bakteria mati ketika tindakbalas hidrotermal, sebelum sampel ini

dipanaskan pada 500 °C. Keputusan-keputusan yang diperoleh ini telah mendedahkan bahawa pembentukan struktur nano/mikrostruktur ZnO banyak bergantung kepada kawasan di mana spesis zink menempel pada organel bakteria dan kuantiti larutan ion zink yang diletakkan ke dalam sistem larutan ampaian bakteria.

Topik lain yang juga dikaji dalam kajian ini adalah kajian ke atas sifat agrgasi/aglomerasi partikel ZnO di dalam filem komposit ZnO/PVA tanpa menggunakan agen penyadur organik. Beberapa nisbah jisim filem komposit ZnO/polimer telah disediakan melalui kaedah larutan kasting dengan menggunakan komersil partikel ZnO dan polimer larut-air, polivinil alkohol (PVA). Penyiasatan ke atas ciri-ciri optik, terma, dan mekanikal termasuk kemungkinan partikel ZnO boleh disebar secara homogenos dalam matriks polimer telah dilakukan. Analisis terma (TGA-DTG, DSC) menunjukkan bahawa keseimbangan terma bagi polimer PVA merosot setelah dimasukkan partikel ZnO dan kesannya semakin ketara apabila kuantiti ZnO yang dimasukkan ditambah. XRD bagi filem komposit ZnO/PVA memperlihatkan bahawa kekuatan pembelauan bagi fasa ZnO dan PVA berubah mengikut perubahan agregasi partikel apabila kuantiti ZnO dan PVA yang terlibat diubah. Manakala nilai tenaga leluang jalur, E_g yang ditentukan daripada spectra UV-Vis mengalami penurunan apabila kuantiti ZnO dan PVA ditambah. Hal ini adalah disebabkan partikel-partikel ZnO yang besar terbentuk akibat kecenderungan partikel untuk beragregasi tinggi. Selain itu, kemungkinan partikel ZnO boleh disebarkan di dalam matriks PVA adalah tinggi pada kuantiti ZnO dan PVA yang amat rendah setelah dilakukan pencirian ESEM dan TEM ke atas sampel nisbah jisim ZnO:PVA, 1:30 di dalam matriks 1% PVA.

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I certify that a Thesis Examination Committee has met on **25 February 2011** to conduct the final examination of Wan Haizum Binti Wan Nor Azmin on her thesis entitled "**Synthesis and Physicochemical Investigations of Templated and Composite Zinc Oxide**" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Examination Committee are as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of **Master of Science**. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

WAN HAIZUM BINTI WAN NOR AZMIN

Date: 25 February 2011

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